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(21) International Application Number: PCT/AU96/00466 (22) International Filing Date: 25 July 1996 (25.07.96) (30) Priority Data: PN 4436 28 July 1995 (28.07.95) AU (71) Applicant (for all designated States except US): SOLA INTERNATIONAL HOLDINGS LTD. [AU/AU]; Sherriffs Road, Lonsdale, S.A. 5160 (AU). (72) Inventors; and (75) Inventors/Applicants (for US only): TOH, Huan, Kiak [MY/AU]; 24 Medway Street, Fullerton, S.A. 5063 (AU). CHEN, Fang [AU/AU]; 20 Nalimba Street, Hallett Cove, S.A. 5158 (AU). (74) Agent: PHILLIPS ORMONDE & FITZPATRICK; 367 Collins Street, Melbourne, VIC 3000 (AU).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i>
(54) Title: PHOTOCHROMIC POLYMER <div style="text-align: center; margin: 20px 0;"> $P-(S)_n-R \quad (1)$ </div> (57) Abstract <p>A photochromic monomer having formula (1), wherein n is an integer of 0 to 5; P is a photochromic dye moiety or derivative thereof; S is an organic spacer group; and R is a polymerisable group.</p>		

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PHOTOCHROMIC POLYMER

The present invention relates to the manufacture of plastic optical articles such as video discs, ophthalmic lenses and the like. In particular, the present invention relates to photochromic monomers and the manufacture of
5 photochromic optical articles incorporating same.

It has been suggested in the prior art to use a number of approaches to incorporate photochromic compounds into a synthetic polymeric host material.

For example, United States Patent No. 3,212,898 describes preparing a photosensitive composition by suspending a photochromic benzospiropyran in a
10 preformed polyester resin. United States Patent No. 3,666,352 describes dispersing a mercury thiocarbazon compound in a solidified plasticised vinyl chloride-vinyl acetate copolymer, which copolymer is laminated between two plastic or glass layers, thereby to form a photochromic sunglass lens.

Bulk dyed photochromic plastic lenses, that is where photochromic
15 molecules are dispersed throughout the lens, are difficult to use for ophthalmic purposes because the photochromic performance of the plastic is very dependant on temperature. Whilst this same effect occurs to a degree with photochromic glass lenses, it is not as noticeable.

Accordingly, conventional wisdom in the prior art indicates that organic
20 photochromic dyes must be provided in regions or zones of constant thickness, independent of the optical geometry of the lens. Surface imbibition is the only commercial process for achieving a satisfactory product.

However, surface imbibition is a costly process and such lenses are in
25 turn available only from specialist sources and are not freely available to the public.

Particular difficulties which have been encountered in the prior art when attempts have been made to incorporate photochromic material prior to the formation of a photochromic optical article include uneven colouration caused by the variable thickness of the lens which is required to provide the lens with the
30 necessary optical power.

Further, for example as described in United States 5,130,353 or United States 5,185,390, the prior art describes the inclusion of photochromic dyes into

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the subsurface regions of a plastic lens by first positioning a polymeric or other carrier of photochromic dye physically against the surface of the lens and then using heat (in the range 100 to 150°C) to cause the dyes to undergo sorption and diffuse into the lens. The depleted carrier is removed from the lens after the

5 passage of sufficient time at elevated temperature, typically of order 1/2 to 4 hours. It is found that adequate darkening is achieved with inclusion of 5 to 10 mgm/mm² of surface diffused to a depth of about 50 µm. The average dye concentration in this region of the lens is in the range of 0.1 to 0.2 mgm/mm³, or 7 to 14% (w/w) of the polymer weight in that region.

10 For this procedure to operate effectively, the carrier must accommodate a sufficient concentration of dye in sufficient volume to deliver the required level of dopant. Commonly, carrier films are in the range 50 to 80 µm thick. The intensity and duration of the heating step should be sufficient to obtain thermal transfer by permeation of the dyes without decomposing them or causing significant

15 softening of the host polymer (lens). Either decomposition or softening will result in lenses being rejected.

An alternative approach is to include the dyes within an optical coating resin and applying the coating to the lens directly. Optical coatings thus applied are rarely thicker than 10 µm because of declining optical quality and the

20 magnification of stresses caused by differential shrinkage of thick coatings. Because of this thickness limitation, the optical density achieved by this approach falls well short of the target levels. Hence, it would be a significant advance in the art if an alternative process could be devised to minimise or avoid the effect that elevated temperature has upon both the dyes and the polymer.

25 It is accordingly an object of the present invention to overcome or at least alleviate one or more of the difficulties and deficiencies related to the prior art.

Accordingly, in a first aspect of the present invention there is provided a photochromic monomer having the formula



30 wherein

n is an integer of 0 to 5;

P is a photochromic dye moiety or derivative thereof;

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S is an organic spacer group; and

R is a polymerisable group.

The photochromic monomer according to this aspect may be incorporated in a cross-linking polymeric casting composition directly, or may be incorporated in a thin layer coating composition. Applicant has surprisingly found that when the photochromic monomer according to this aspect of the invention is incorporated into a cross-linking polymeric casting composition, the photochromic material has a reduced sensitivity to temperature. The utilisation of the photochromic monomer may eliminate the necessity for a separate photochromic process on an optical article.

The photochromic dye moiety or derivative P may be of any suitable type. An hydroxy derivative may be used. P may be derived from a photochromic dye selected from one or more of the group consisting of anthraquinones, phthalocyanines, spiro-oxazines, chromenes, pyrans including spiro-pyrans and fulgides. A spiro-oxazine residue is preferred.

Preferred photochromic dyes may be selected from the group consisting of

- 1,3-dihydrospiro[2H-anthra[2,3-d]imidazole-2,1'-cyclohexane]-5,10-dione
- 1,3-dihydrospiro[2H-anthra[2,3-d]imidazole-2,1'-cyclohexane]-6,11-dione
- 20 • 1,3-dihydro-4-(phenylthio)spiro[2H-anthra[1,2-d]imidazole-2,1'-cyclohexane]-6,11-dione
- 1,3-dihydrospiro[2-H-anthra[1,2-d]imidazole-2,1'-cycloheptane]-6,11-dione
- 1,3,3-trimethylspiroindole-2,3'-[3H]naphtho[2,1-b]-1,4-oxazine]
- 1,3,3-trimethyl-9'-hydroxyspiroindolinenaphthoxadine
- 25 • 1,3,3-trimethyl-9'-(2-hydroxyethoxy)-spiroindolinenaphthoxadine
- 1,3,3-trimethyl-6'-piperidino-9'-hydroxy-spiroindolinenaphthoxadine
- 2-methyl-3,3'-spirobi[3H-naphtho[2,1-b]pyran] (2-Me)
- 2-phenyl-3-methyl-7-methoxy-8'-nitrospiro[4H-1-benzopyran-4,3'-[3H]-naphtho[2,1-b]pyran
- 30 • Spiro[2H-1-benzopyran-2,9'-xanthene]
- 8-methoxy-1',3'-dimethylspiro(2H-1-benzopyran-2,2'-(1'H)-quinolin
- 2,2'-Spirobi[2H-1-benzopyran]

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- 5'-amino-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indolin
- Ethyl- β -methyl- β -(3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indolin-1'-yl)-propenoate
- (1,3-propanediyl)bis[3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline]
- 3,3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-benzoxazoline]
- 6'-methylthio-3,3'-dimethyl-8-methoxy-6-nitrospiro[2H-1-benzopyran-2,2'-benzothiozoline]
- (1,2-ethanediyl)bis[8-methoxy-3-methyl-6-nitrospiro[2H-1-benzopyran-2,2'-benzothiozoline]
- N-N'-bis(3,3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-(3'H)-benzothioazol-6'-yl)decanediamide
- α -(2,5-dimethyl-3-furyl)ethylidene(Z)-ethylidenesuccinic anhydride; α -(2,5-dimethyl-3-furyl)- α' , δ -dimethylfulgide
- 2,5-diphenyl-4-(2'-chlorophenyl)imidazole
- [(2',4'-dinitrophenyl)methyl]-1H-benzimidazole
- N-N-diethyl-2-phenyl-2H-phenanthro[9,10-d]imidazol-2-amine
- 2-Nitro-3-aminofluoren-2-amino-4-(2'-furanyl)-6H-1,3-thiazine-6-thione

The selection of photochromic dye moiety which may be used may extend to conventional tinting dyes.

The polymerisable group R may be any reactive group capable of forming a polymer. An ethyleneically unsaturated group is preferred. An olefinic, allylic, polythiol, vinyl, acrylic or polyisocyanate group may be used. An acrylic or methacrylic group is preferred. An acrylate or methacrylate ester may be used.

The polymerisable group R may function to improve the solubility of the photochromic monomer in the monomer mix.

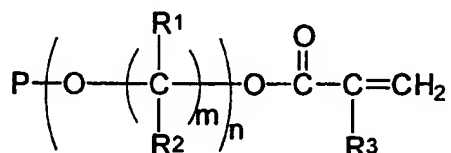
The organic spacer group S, when present, may be of any suitable type. The group S may be selected from the group consisting of

- alkyl of 1 to 25 carbon atoms, preferably 1 to 6 carbon atoms;
 - alkoxy of 1 to 25 carbon atoms, preferably 1 to 6 carbon atoms; and
 - aryl or heterocyclic groups of 5 to 10 carbon atoms;
- with or without substituents selected from halogen, hydroxy, amine, acyl or

carbonyl groups.

The organic spacer group S may function to further improve the solubility of the photochromic monomer in the monomer mix, where required.

- A preferred photochromic monomer is selected from the group consisting
- 5 of an ethoxy methacrylate derivative of 1,3-dihydrospiro[2H-anthra[2,3-d]imidazole-2,1'-cyclohexane]-5,10-dione, an acrylate derivative of 1,3,3-trimethyl-9'-hydroxyspiroindolinenaphthoxadine, a methacrylate derivative of 1,3,3-trimethyl-9'-(2-hydroxyethyloxy)-spiroindolinenaphthoxadine and an acrylate derivative of 1,3,3-trimethyl-6'-piperidino-9'-hydroxyspiroindolinenaphthoxadine.
- 10 In a preferred aspect of the present invention there is provided a photochromic monomer having the formula



wherein

- P is a photochromic dye derivative from a photochromic dye selected
- 15 from one or more of the group consisting of anthraquinones, phthalocyanines, spiro-oxazines, chromenes, pyrans including spiro-pyrans and fulgides;

n is an integer of 0 to 5;

m is an integer of 1 to 10;

- R¹ and R², which may be the same or different, are selected from
- 20 hydrogen, halogen and an alkyl or substituted alkyl of 1 to 10 carbon atoms, or

$\text{---} \left(\overset{\overset{R^1}{|}}{\underset{\underset{R^2}{|}}{C}} \right)_m \text{---}$ is an aryl or heterocyclic group of 5 to 10 carbon atoms; and

R³ is selected from hydrogen, halogen, alkyl or substituted alkyl of 1 to 10 carbon atoms or alkoxy, or substituted alkoxy or 1 to 10 carbon atoms.

- Preferably, R¹, R² and R³ are selected from the group consisting of
- 25 hydrogen and alkyl or 1 to 5 carbon atoms.

In a particularly preferred aspect the photochromic monomer may function as a polymeric switch. The polymeric switch may be activated by the action of ultraviolet (UV) light on the photochromic dye moiety P. Accordingly the photochromic monomer may have the formula



wh rein

n and p are each integers of 0 to 5;

P is a photochromic dye moiety or derivative thereof;

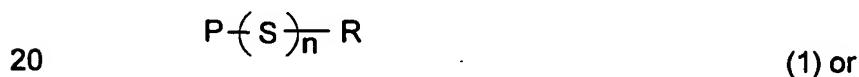
5 S and S', which may be the same or different, are each an organic spacer group;

R and R', which may be the same or different, are each a polymerisable group.

It will be understood that the action of ultraviolet light of the photochromic monomer in this embodiment is as follows. The UV light functions to activate the photochromic dye moiety P which in turn undergoes a ring opening or other stereo transformation. This will affect the bulk properties of the polymer because of the presence of P in the polymer backbone. Properties which may be affected include density, rigidity, Tg, modulus, etc., optical properties, e.g. colour, transmission, refractive index and transparency, and chemical properties, e.g. swelling or dye uptake.

In a further aspect of the present invention there is provided a cross-linkable polymeric casting composition including

a photochromic monomer of the formula



wherein

n and p are each integers of 0 to 5;

P is a photochromic dye moiety or derivative thereof;

25 S and S', which may be the same or different, are each an organic spacer group;

R and R', which may be the same or different, are each a polymerisable group;

a diacrylate or dimethacrylate monomer; and

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a polymerisable comonomer.

The cross-linkable polymer casting composition may be utilised to produce a photochromic optical article such as an optical lens.

The photochromic monomer may be present in amounts of from
5 approximately 0.001 to 55% by weight, preferably approximately 0.01 to 5% by weight, based on the total weight of the casting composition. If solubility problems are encountered at higher concentrations of photochromic monomer these may be overcome by the use of spacers.

The diacrylate or dimethacrylate monomer in the polymeric casting
10 composition may be a polyoxyalkylene glycol diacrylate or dimethacrylate, for example a polyethylene glycol dimethacrylate with an average molecular weight of approximately 600.

The polyoxy alkylene glycol diacrylate or dimethacrylate compound may include ethylene oxide or propylene oxide repeating units in its backbone. A
15 polyethylene glycol dimethacrylate is preferred. One suitable material is that sold under the trade name NKESTER 9G by Shin Nakamura. Alternatively, or in addition, an NK Ester 6G, 4G or 14G may be used.

The polyoxy alkylene glycol diacrylate or dimethacrylate component may be present in amounts of from approximately 5% by weight to 60% by weight,
20 preferably approximately 30% to 50% by weight, based on the total weight of the casting composition.

The polymerisable comonomer may be selected to improve the properties and/or processability of the cross-linkable polymeric casting composition. The polymerisable comonomer may be selected from any suitable type, e.g.
25 methacrylates, acrylates, vinyls, vinyl ethers, allyls, aromatic olefins, ethers, polythiols, epoxies and the like.

The polymerisable comonomer may be a low viscosity comonomer. The low viscosity comonomer may be of any suitable type. The low viscosity comonomer may be selected from one or more of aromatic olefins, polymerisable
30 bisphenol monomers capable of forming a homopolymer having a high refractive index of more than 1.55, urethane monomers having 2 to 6 terminal acrylic or methacrylic groups, and thiodiacrylate or dimethacrylate monomers.

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The aromatic olefins may be selected from styrene, divinyl benzene and 3,9-divinyl-2,4,8,10-tetraoxaspiro [5.5]undecane (DTU). The aromatic olefins may be present in amounts of approximately 5 to 50% by weight.

5 The polymerisable bisphenol monomer may be a high index bisphenol monomer.

The high index bisphenol monomer component in the cross-linkable casting composition may be selected from: dimethacrylate and diacrylate esters of bisphenol A dimethacrylate and diacrylate esters of 4,4'-bishydroxyethoxy-bisphenol A and the like.

10 Preferred high index bisphenol compounds include bisphenol A ethoxylated dimethacrylate and tetra brominated bisphenol A ethoxylated dimethacrylates. A bisphenol A ethoxylate dimethacrylate sold under the trade designation ATM 20 by Ancomer has been found to be suitable.

15 The high index bisphenol monomer may be present in amounts of from approximately 10 to 60% by weight, preferably 20 to 55% by weight, based on the total weight of the casting composition.

As stated above, the polymerisable comonomer may include a urethane monomer having 2 to 6 terminal acrylic and/or methacrylic groups. Suitable materials falling within this definition include materials supplied under the trade names U-4H, U-4HA and U-6HA by Shin Nakamura, NF-201 and NF-202 by Mitsubishi Rayon.

The urethane monomer may be present in amounts of from approximately 2.5% to approximately 35% by weight, preferably 5% to 25% by weight, based on the total weight of the casting composition.

25 The thiodiacrylate or dimethacrylates may be selected from bis(4-methacryloylthioethyl)sulfide (BMTES) and bis(4-methacryloylthiophenyl)sulfide (BMTS or TS). The thiodiacrylate may be present in amounts of from approximately 5 to 40% by weight, preferably 20 to 40% by weight.

30 In a preferred aspect of the present invention the cross-linkable polymeric coating composition may further include at least one poly-functional unsaturated cross-linking agent.

The poly functional unsaturated cross-linking agent according to the

present invention may be a tri- or tetra- functional vinyl, an acrylic or methacrylic monomer. The cross-linking agent may be a short chain monomer for example trimethylol propane trimethacrylate, pentaerythritol triacrylate or tetracrylate, or the like. Other polyfunctional cross-linking agents which may be used include NK Ester TMPT, NK Ester A-TMPT, NK Ester A-TMM-3, NK Ester A-TMMT, di-trimethylol propane tetraacrylate, trimethylolpropane triacrylate, pentaerythritol tetramethacrylate, dipentaerythritol monohydroxypenta acrylate, pentaerythritol triacrylate, ethoxylated trimethylolpropane triacrylate, ethoxylated trimethylolpropane trimethacrylate.

- 10 The polyfunctional unsaturated cross-linking agent may be present in amounts of from approximately 5 to 45% by weight, preferably approximately 30 to 40% by weight based on the total weight of the casting composition.

The cross-linkable casting composition may further include a co-reactant including a polythiol.

- 15 The polythiol may be selected from the group consisting of Pentaerythritol Tetrakis (3-mercapto- propionate) [PTMP], Trimethylolpropane Tris (3-mercapto-propionate) [TTMP], 4-mercaptomethyl-3,6-dithia-1,8-octanedithiol [MDO], Pentaerythritol Tetrakis (3-mercaptoacetate) [PTMA], Trimethylolpropane Tris (3-mercaptoacetate) [TTMA], 4-t-butyl-1,2-benzenedithiol, 2-mercaptoethylsulfide, 20 4,4'-thiodibenzenethiol, benzenedithiol, Glycol Dimercaptoacetate, Glycol Dimercaptopropionate Ethylene bis(3-Mercaptopropionate), Polyethylene Glycol Dimercaptoacetates, Polyethylene Glycol Di(3-Mercaptopropionates).

The thiol compound may be present in amounts from 0 to approximately 50% by weight.

- 25 The cross-linkable casting composition according to the present invention may further include an initiator. The initiator may be a heat and/or ultraviolet (U.V.) initiator. A cationic initiator may be used where epoxies are incorporated in the composition. A photoinitiator, preferably a long wavelength photoinitiator, may be used in combination with a cure modifier to provide a UV absorbing 30 material.

The amount of curing agent may vary with the monomers selected. It has been possible to operate with a relatively low level of curing agent of between

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approximately 0.05 and 1.5%, preferably 0.4% to 1.0% by weight.

The following curing agents have been found to be suitable.

AIBN (Azo radical heat initiator)

Azodiisobutyronitrile

- 5 • Trigonox TX-29 (Dialkyl Peroxide radical heat initiator)
1,1-di-(*n*-butyl peroxy-3,3,5-trimethyl cyclohexane)
- TBPEH (Alkyl Perester radical heat initiator)
t-butyl per-2-ethylhexanoate
- (Diacyl Peroxide radical heat initiator)
- 10 Benzoyl Peroxide
- (Peroxy Dicarboxate radical heat initiator)
Ethyl Hexyl Percarbonate
- (Ketone Peroxide radical heat initiator)
Methyl ethyl ketone peroxide
- 15 • Cyracure UV1-6974 (cationic photoinitiator)
Triaryl sulfonium hexafluoroantimonate
- Lucirin TPO (radical photoinitiator)
2,4,6-Trimethylbenzoyldiphenylphosphine oxide
- Vicure 55 (radical photoinitiator)
- 20 methyl phenylglyoxylate
- Bis(*t*-butyl peroxide) diisopropylbenzene
- *t*-butyl perbenzoate
- *t*-butyl peroxy neodecanoate
- Amicure DBU
- 25 • Amicure BDMA
- DABCO
- Amicure DBU and/or Amicure BDMA are preferred.

Initiator may be a single component or combination of initiator components.

- 30 The photochromic optical article formed from the cross-linkable casting composition according to the present invention may be light-transmissible. The

optical article may be transparent.

The photochromic optical article may exhibit a high refractive index. The optical article may also retain good abrasion resistance and impact resistance, and reduced fatigue.

- 5 Other additives may be present which are conventionally used in casting compositions such as inhibitors, dyes, UV stabilisers and materials capable of modifying refractive index. Mould release agents can be added but they are in general not required with the compositions used in the method of the present invention. Such additives may include:

10 UV Absorbers including

- Ciba Geigy Tinuvin P - 2(2'-hydroxy-5'methyl phenyl) benzotriazole
- Cyanamid Cyasorb UV 531 -2-hydroxy-4-n-octoxybenzo- phenone
- Cyanamid Cyasorb UV5411-2(2-hydroxy-5-t-octylphenyl)- benzotriazole
- Cyanamid UV 2098 - 2 hydroxy-4-(2-acryloyloxyethoxy) benzophenone
- 15 • National Starch and Chemicals Permasorb MA - 2 hydroxy-4-(2 hydroxy-3-methacryloxy)propoxy benzophenone
- Cyanamid UV24 - 2,2'-dihydroxy-4-methoxybenzophenone
- BASF UVINUL 400 - 2,4 dihydroxy-benzophenone
- BASF UVINUL D-49 - 2,2'-dihydroxy-4,4' dimethoxy- benzophenone
- 20 • BASF UVINUL D-50 - 2,2', 4,4' tetrahydroxy benzophenone
- BASF UVINUL D-35-ethyl-2-cyano-3,3-diphenyl acrylate
- BASF UVINUL N-539-2-ethexyl-2-cyano-3,3-diphenyl acrylate
- Ciba Geigy Tinuvin 213

Hindered amine light stabilisers (HALS), including

- 25 • Ciba Geigy Tinuvin 765/292 - bis (1,2,2,6,6-penta- methyl-4-piperidyl)sebacate
- Ciba Geigy 770 - bis (2,2,6,6-tetramethyl-4- piperidiny)l sebacate

Antioxidants including

- 30 • Ciba Geigy Irganox 245 - triethylene glycol-bis-3- (3-tertbutyl-4-hydroxy-5-methyl phenyl)propionate
- Irganox 1010 -2,2-bis[[3-[3,4-bis(1,1-dimethyl- thyl)-4-hydroxyphenyl]-1-oxopropoxy]methyl]-1,3- propanediyl 3,5-bis(1,1-dimethyl ethyl)-4-hydroxy

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benzen propanoate

- Irganox 1076 - octadecyl 3-(3',5'-di-tert-butyl(-4'- hydroxyph nyl) propionate

Anticolouring agents including

- Triphenyl phosphine
- 5 • 10 dihydro-9-oxa-10-phosphaphenanthrene-1-oxide

Cure modifiers including

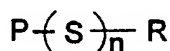
- Dodecyl mercaptan
 - PTMP - pentaerythritol tetrakis (3-mercapto propionate)
 - Butyl mercaptan
- 10 • Bis-GHA
- Thiophenol
 - Nofmer from Nippon Oils and Fats
 - Q1301 from Waco

Other monomeric additives can be present in amounts up to 10% by
 15 weight as diluents, and include monomers such as methacrylic acid, vinyl silanes, methyl allyl, hydroxy ethyl, methacrylate and materials containing hydroxy, amino and phosphine oxide groups. Other monomeric additives may be included to improve processing and/or material properties, these include:

- methacrylic acid, maleic anhydride, acrylic acid
- 20 • adhesion promoters/modifiers such as Sartomer 9008, Sartomer 9013, Sartomer 9015 etc.
- dye-enhancing, pH-adjusting monomers like Alcolac SIPOMER 2MIM
 - a charge-reducing cationic monomer to render the material more antistatic, example Sipomer Q5-80 or Q9-75
- 25 • hydrophobic comonomers: Shin Nakamura NPG, P9-G etc. to reduce the water adsorption of the material
- viscosity modifiers

In a further aspect of the present invention there is provided a
 photochromic optical article formed from

30 a cross linkable casting composition including
 a photochromic monomer of the formula



(1) or

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wherein

n and p are each integers of 0 to 5;

P is a photochromic dye moiety or derivative thereof;

5 S and S', which may be the same or different, are each an organic spacer group;

R and R', which may be the same or different, are each a polymerisable group;

a diacrylate or dimethacrylate monomer; and

10 a polymerisable comonomer.

The optical article may provide characteristics substantially equal to or greater than those achievable with industry standard optical articles, but with reduced stress/strain and reduced yellowing.

15 The overall refractive index may be in the mid refractive index range of from approximately 1.51 to 1.57, preferably 1.53 to 1.57.

The optical articles prepared by the method of this invention include camera lenses, ophthalmic lenses and video discs.

20 The casting composition may be formed into an optical article by mixing in a convenient vessel the components making up the material, and then adding the photo-initiator. The mixed material is then degassed or filtered.

The photochromic dye moiety may be selected from one or more of the group consisting of anthraquinones, phthalocyanines, spiro-oxazines, chromenes, pyrans and fulgides. The photochromic dye layer or coating may exhibit reduced fatigue.

25 The photochromic monomer may alternatively be incorporated in a coating applied to an optical article.

In an alternative preferred aspect, there is provided a photochromic coating composition including

a photochromic monomer of the formula





wherein

n and p are each integers of 0 to 5;

P is a photochromic dye moiety or derivative thereof;

5 S and S', which may be the same or different, are each an organic spacer group;

R and R', which may be the same or different, are a polymerisable group;

a polymerisable co-monomer; and

10 a solvent therefor.

The photochromic monomer may be present in amounts of from approximately 0.5 to 25% by weight, preferably approximately 0.5 to 10% by weight, based on the total weight of the coating composition, excluding solvent.

The photochromic coating composition may be UV curable.

15 The polymerisable co-monomer may be a UV curable monomer.

A low shrinkage monomer may be used. A siloxane monomer may be used. γ -methacryloxypropyl trimethoxy silane has been found to be suitable. An acrylate-terminated oligomer may be used. An acrylate-terminated urethane or epoxy oligomer may be used. The oligomer may be selected from one or more of

20 the following:

- Epoxy acrylates
- Acrylated epoxidised oils
- Aromatic urethane acrylates
- Aliphatic urethane acrylates
- 25 • Polyester acrylates
- Acrylated melamine
- Acrylated amines
- Acrylamidomethyl cellulose
- Acrylated polybutadiene
- 30 • Aliphatic polyol acrylates
- Polyether acrylates

The polymerisable co-monomer may be present in amounts of from approximately 65% to 95% by weight, preferably approximately 80% to 95% by weight, based on the total weight of the coating composition, excluding solvent.

An acrylic or acrylate diluent may be included. The acrylate diluent may

- 5 be selected from the following:
- POPETA Propylated pentaerythritol acrylate
 - TMPTA Trimethylolpropane triacrylate
 - EOTMPTA Ethoxylated trimethylolpropane triacrylate
 - POTMPTA Propoxylated trimethylolpropane triacrylate
 - 10 • HDODA Hexanediol diacrylate
 - EONPGDA Ethoxylated neopentyl glycol diacrylate
 - PONPGDA Propoxylated neopentyl glycol diacrylate
 - TEGDA Tetraethylene glycol diacrylate
 - TPDGA Tripropylene glycol diacrylate
 - 15 • TPGMEA Tripropylene glycol methyl ether acrylate
 - NPGDA Neopentyl glycol diacrylate
 - BDDA 1,4-butanediol diacrylate
 - DMPA α,α -dimethoxy- α -phenylacetophenone
 - DEGDA di-ethylene glycol diacrylate
 - 20 • EHA 2-ethylhexyl acrylate
 - HDDA 1,6-hexanediol diacrylate
 - HEBDM bis(2-hydroxyethyl)bisphenol-A dimethacrylate
 - MMA methyl methacrylate
 - n-PA n-propyl acrylate

- 25 The diluent may be present in amounts of from 0 to approximately 35% by weight, preferably approximately 10% to 30% by weight, based on the total weight of the coating composition, excluding solvent.

The solvent component may be an aqueous or organic solvent. An organic solvent such as ethanol or toluene is preferred.

- 30 The photochromic monomer and polymerisable co-monomer may be present in the coating composition in amounts similar to those specified above.

Accordingly in a further aspect of the present invention there is provided a

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coated optical article including
an optical substrate; and

a polymeric coating adhered to a portion of the optical substrate, the polymeric coating being formed from a photochromic coating composition as
5 described above.

The polymeric coating is formed from a polymeric coating composition of the type described above.

The optical substrate may be a lens, lens wafer, or lens blank. The optical substrate may be formed from the same polymeric material as, or different to, the
10 polymeric material used in the polymeric coating.

The polymeric material utilised in the manufacture of the lens or lens blank may be of any suitable type. A polycarbonate material may be used. An optical material of the allyl diglycol carbonate type may be used. The optical substrate may be formed from cross-linkable polymeric casting compositions, for
15 example as described in applicant's United States Patent 4,912,155, United States Patent Application No. 07/781,392, Australian Patent Applications 50581/93, 50582/93, European Patent Specification 543149A2, or International Patent Applications PCT/AU95/00845 "Heat Responsive Articles" and PCT/AU95/00851 "Method of Preparing Photochromic Article", the entire
20 disclosures of which are incorporated herein by reference.

In a preferred aspect, the polymeric coating may be cast on the optical article utilising front surface coating techniques. Such techniques are described for example in Australian Patent Application 80556/87 or Australian Patent 648,209 to applicants, the entire disclosures of which are incorporated herein by
25 reference.

The present invention will now be more fully described with reference to the accompanying examples. It should be understood, however, that the description following is illustrative only and should not be taken in any way as a restriction on the generality of the invention described above.

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EXAMPLE 1

An ultraviolet (UV) -curable coating composition of the following formulation was prepared.

		<u>% by weight</u>
5	• Ethoxy methacrylate derivative of 1,3-dihydrospiro [2H-anthra[2,3-d]imidazole-2,1'-cyclohexane]-5,10-dione	7.5
	• Dipentaerythritol hexacrylate	10.1
	• TMPTA	10.1
	• DEGDA	5.1
10	• γ -Methacryloyloxypropyl trimethyl silane	25
	• Toluene	21
	• Ethyl acetate	20.5
	• TPO Lucirin (UV initiator)	0.2
	• Nofmer - MSD (2,4-diphenyl-4-methyl-1-pentene)	0.5

15

A commercial middle index plastic lens for example a Spectralite-type lens, was dip coated in the formulation, heat dried and UV cured to give a photochromic film of good durability.

EXAMPLE 2

20 An ultraviolet (UV) curable coating composition of the following formulation was prepared.

		<u>% by weight</u>
	• Dipentaerythritol hexacrylate	30
	• N-Cyclohexylmalimide	6.5
25	• Ethoxy methacrylate derivative of 1,3-dihydrospiro [2H-anthra[2,3-d]imidazole-2,1'-cyclohexane]-5,10-dione	8.2
	• Toluene	55
	• TPO Lucirin (UV initiator)	0.2
	• FC-30 (levelling agent)	0.10

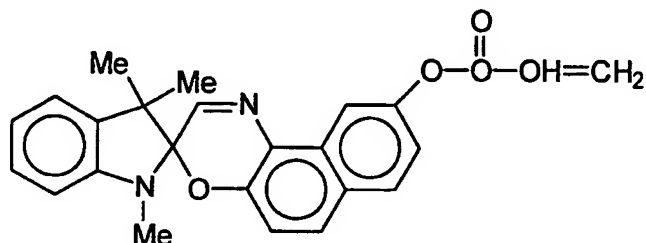
30

The coating formulating was cast on a CR39-type lens utilising front surface coating techniques and UV cured. A photochromic coating of good

durability was produced.

EXAMPLE 3

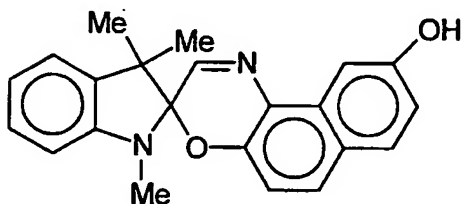
Synthesis of the acrylate derivative of 1,3,3-trimethyl-9'-hydroxyspiroindolenaphthoxadine



5

Photochromic Monomer

7.6g (22 mmol) of 1,3,3-trimethyl-9'-hydroxyspiroindolenaphthoxadine



Dye II

and 3.04 g (30 mmol) of triethylamine were dissolved into 800 ml dichloromethane (previously dried). 2.72 g acryloyl chloride in 20 ml dried dichloromethane was added in dropwise. After 1 hour stirring at room temperature after addition, the solution was poured into 800 ml water. The organic layer was separated and washed once with 5% NaOH aqueous solution and twice with water. The organic layer was dried over anhydrous MgSO_4 . Removal of solvent gave a solid. The solid was recrystallised twice from ethylacetate/petroleum ether (60-80°C) mixture solvent producing 6.5 g of white crystals.

The nuclear magnetic resonance (NMR) spectroscopic analysis was as follows:

$^1\text{H-NMR}(\text{CDCl}_3)$

δ : 1.34 (s, 6H), 2.76 (s, 3H), 6.03 (m, 1H), 6.40 (m, 1H), 6.59-6.69 (m, 2H), 6.87-7.25 (m, 5H), 7.64-7.78 (m, 3H), 8.28 (d, 1H).

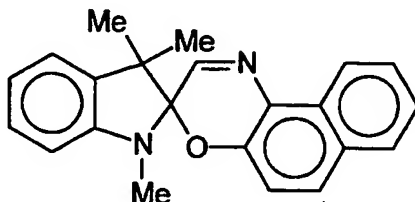
IR: 1738 cm^{-1}

The IR spectrum of the photochromic dye is shown in Figure 1.

The solubility of the polymerisable dye in a standard commercial

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polymeric lens casting composition was improved compared with the base compound 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]phenanthr[9,10-6][1,4]oxazine].



Dye I

- 5 The photochromic monomer is colourless, while 1,3-dihydro-1,3,3-trimethylspiro[2H-indole-2,3'-[3H]phenanthr[9,10-6][1,4]oxazine is coloured even in the dark which limits the amount of dye which may be incorporated in a lens.

EXAMPLE 4

- 10 A heat curable cross-linkable casting composition of the following formulation was prepared.

		<u>% by weight</u>
	• Acrylate derivative of 1,3,3- trimethyl-9'-hydroxyspiroindolinenaphthoxadine	.05
	• Ethoxylated bis-phenol A dimethacrylate (ATM 20)	49.8
15	• Urethane acrylate (U4HA)	5
	• Polyethylene glycol dimethacrylate (9G)	44.95
	• TBPEH (Alkyl Perester radical heat initiator)	0.2

- 20 The monomer mix was prepared in a beaker together with the TBPEH thermal initiator.

The casting material was used to fill the space between a pair of glass moulds separated by a plastic gasket at their periphery and held together by a clip. Cure time was 8 hours with heating at a temperature of 40 to 120°C.

- 25 A satisfactory lens was formed. The lens exhibited an improvement in thermal stability relative to comparable lenses with standard photochromic dyes of approximately 30% as discussed below.

EXAMPLE 5

Example 4 was repeated, but substituting 0.1% of a Lucirin TPO photoinitiator for the TBPEH thermal initiator.

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The mould enclosing the casting material was passed four times under a UV lamp. Cure time was four hours. A satisfactory lens was again formed. The lens exhibited an improvement in thermal stability relative to comparable lenses with standard photochromic dyes of approximately 30% as discussed below.

5

EXAMPLE 6

Example 4 was repeated with an increased level of photochromic dye monomer of 0.2%. A similar satisfactory lens, but with a deeper colour on activation, was produced. This illustrates the increased solubility of the photochromic dye monomer in the monomer mix.

10

EXAMPLE 7

Example 1 was repeated with a UV curable coating composition of the following formulation.

	<u>% by weight</u>
• Commercial UV-curable hard coating composition supplied by Toyobo)	98
• Acrylate derivative of 1,3,3-trimethyl-9'-hydroxyspiroindolenaphthoxadine	2

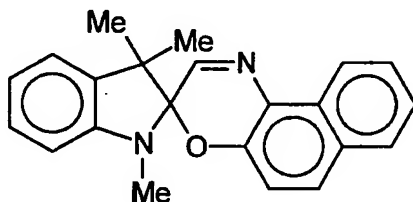
A Spectralite-type lens was dip coated in the formulation, heat dried and UV cured to give a photochromic film of good durability. The improved solubility of the acrylate derivative permits incorporation of increased amounts of photochromic dye via the route.

20

COMPARATIVE EXAMPLE 1

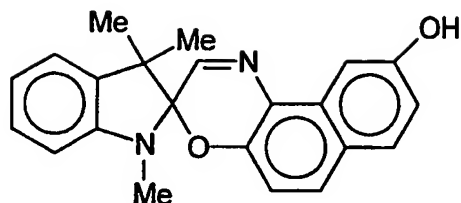
Example 4 was repeated substituting dye I and dye II below for the photochromic dye monomer according to the present invention.

25



Dye I

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Dye II

Thermal stability of all three lenses was calculated by measuring transmittance before and after exposure of the lenses to illumination to activate the photochromic effect.

- 5 The measurements were undertaken at 23°C and 35°C in each case. The results are shown in Figures 2 to 13. Xenon Intensity in each case was 50 kix. Each graph shows a darkening phase followed by a fade back phase.

The results are summarised in Table 1 below.

TABLE 1

10 0.05% photochromic dye in the lens

	Lens Bearing Dye I	Lens Bearing Dye II	Lens Bearing Photochromic Monomer
Max change in transmittance 23°C	29.9%	29.2%	28.2%
Max change in transmittance 35°C	12.0%	10.8%	16.1%
difference between two temperatures	17.9%	18.4%	12.1%

0.2% photochromic dye in the lens

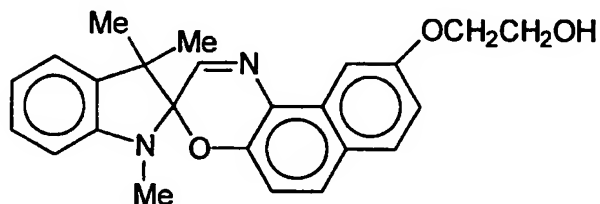
	Lens Bearing Dye I	Lens Bearing Photochromic Monomer (Heat Cured)	Lens Bearing Photochromic Monomer (UV Cured)
Max change in transmittance 23°C	35%	30.4%	31.9%
Max change in transmittance 35°C	16%	17.8%	17.1%
difference between two temperatures	19%	12.6%	14.8%

Tabl 1 illustrates the increased thermal stability of the lens utilising the photochromic monomer according to the present invention.

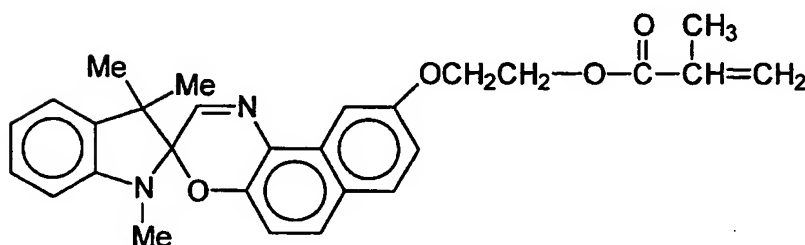
EXAMPLE 8

Synthesis of Methacrylate Derivative of 1,3,3-trimethyl-9'-(2-hydroxyethoxy)-spiroindoline naphthoxadine

5



Dye III

Photochromic
Monomer IV

- 10 8.54 g (22 mmol) of III and 3.04 g (30 mmol) triethylamine were dissolved into 800 ml dichloromethane (previously dried over anhydrous MgSO_4). 3.45 g (30 mmol) of methacryloyl chloride in 20 ml dried dichloromethane was added in dropwise at 0°C . After addition the solution was stirred at room temperature for 1 hour, then poured into 800 ml water. The organic layer was separated and
- 15 washed once with 5% NaOH aqueous solution, once with 5% HCl aqueous solution and twice with water. After drying with anhydrous MgSO_4 , the solvent was removed to give a solid. The solid was twice recrystallised from petroleum ether (60°C to 80°C) to produce 5.0 g of crystalline solid.

The NMR spectroscopic analysis was as follows:

20

$^1\text{H-NMR}$ (CDCl_3)

δ : 1.34 (s, 6H), 1.95 (s, 3H), 2.76 (s, 3H), 3.85 (t, 2H), 4.28 (t, 2H), 5.60 (s, 1H), 6.15 (s, 1H), 6.40-8.30 (10H).

IR: 1738 cm⁻¹

EXAMPLE 9

Example 4 was repeated substituting the methacrylate derivative of 1,3,3-trimethyl-9'-(2-hydroxyethyloxy)-spiroindolinenaphthoxadine prepared in Example 5 7 in place of the acrylate derivative of 1,3,3-trimethyl-9'-hydroxyspiroindolinenaphthoxadine.

A satisfactory lens was formed. The lens exhibited an improvement in thermal stability relative to comparable lenses with standard photochromic dyes of approximately 20% as discussed below.

10

COMPARATIVE EXAMPLE 2

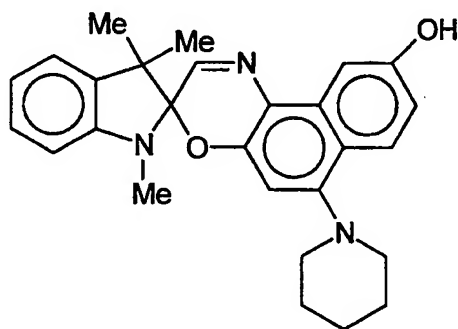
Example 9 was repeated substituting dye III for the photochromic monomer IV.

Thermal stability was analysed as described in comparative Example 1 above. The lens of Example 8 exhibited a significantly better thermostability than 15 the lens produced with dye III.

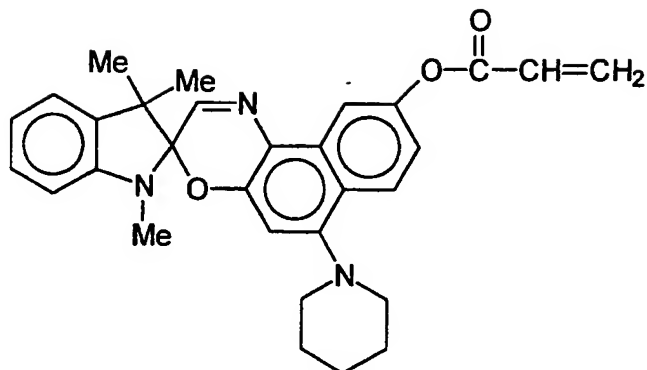
The solubility of monomer IV in the above lens formulation and the commercial hard coating resin supplied by Toyobo is much better than that of 1,3,3-trimethyl-9'-hydroxy-spiroindolinenaphthoxadine.

EXAMPLE 10

20 Synthesis of Acrylate Derivative of 1,3,3-trimethyl-6'-piperidino-9'-hydroxyspiroindolinenaphthoxadine



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Photochromic
Monomer VI

9.42 g (22 mmol) of 1,3,3-trimethyl-6'-piperidino-9'-hydroxyspiroindolinenaphthoxadine and 3.04 g (30 mmol) triethylamine were dissolved into
 5 800 ml dichloromethane (dried over anhydrous MgSO_4). 2.72 g (30 mmol) acryloyl chloride in 20 ml dried dichloromethane was added in dropwise at 0°C . After one hour stirring at room temperature, the solution was poured into 800 ml water. The organic layer was separated and washed once with 5% NaOH aqueous solution, once with 5% HCl aqueous solution and twice with water.
 10 Removal of solvent gave a solid. The solid was recrystallised twice from petroleum ether (60°C to 80°C) gave 4.0 g of crystalline solid.

The NMR spectroscopic analysis was as follows:

$^1\text{H-NMR}$ (CDCl_3) 1.34 (s, 6H), 1.50 (m, 6H), 2.76 (s, 3H), 2.90 (t, 4H),
 6.04 (m, 1H), 6.40 (m, 1H), 6.58-6.68 (m, 2H), 6.80-8.30 (8H)

15 IR: 1738 cm^{-1}

EXAMPLE 11

Example 4 was repeated substituting the acrylate derivative of 1,3,3-trimethyl-9'-hydroxyspiroindolinenaphthoxadine prepared in Example 3 with the acrylate derivative of 1,3,3-trimethyl-6'-piperidino-9'-hydroxyspiroindolinenaphthoxadine prepared in Example 10.
 20

A satisfactory lens was formed. The lens exhibited an improvement in thermal stability relative to comparable lenses with standard photochromic dyes of approximately 30% as discussed below.

COMPARATIVE EXAMPLE 3

25 Example 11 was repeated substituting dye V for the photochromic

monomer VI.

Thermal stability was analysed as described in comparative Example 1 above. The lens of Example 10 exhibited a significantly better thermostability than the lens produced with dye V.

- 5 The solubility of monomer VI, in the above lens formulation and in the commercial hard coating resin supplied by Toyobo, is also much better than that of dye V.

- Finally, it is to be understood that various other modifications and/or alterations may be made without departing from the spirit of the present invention
10 as outlined herein.

Claims

1. A photochromic monomer having a formula

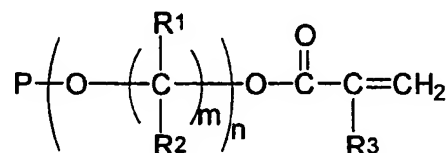


wherein

- 5 n is an integer of 0 to 5;
 P is a photochromic dye moiety or derivative thereof;
 S is an organic spacer group; and
 R is a polymerisable group.
2. A photochromic monomer according to Claim 1 wherein the photochromic
 10 dye moiety or derivative is derived from photochromic dyes selected from one or more of the group consisting of anthraquinones, phthalocyanines, spiro-oxazines, chromenes, pyrans including spiro-pyrans and fulgides.
3. A photochromic monomer according to Claim 2 wherein P is derived from a photochromic dye selected from the group consisting of
- 15 • 1,3-dihydrospiro[2H-anthra[2,3-d]imidazole-2,1'-cyclohexane]-5,10-dione
 • 1,3-dihydrospiro[2H-anthra[2,3-d]imidazole-2,1'-cyclohexane]-6,11-dione
 • 1,3-dihydro-4-(phenylthio)spiro[2H-anthra[1,2-d]imidazole-2,1'-cyclohexane]-6,11-dione
 • 1,3-dihydrospiro[2-H-anthra[1,2-d]imidazole-2,1'-cycloheptane]-6,11-dione
 20 • 1,3,3-trimethylspiro[indole-2,3'-[3H]naphtho[2,1-b]-1,4-oxazine]
 • 1,3,3-trimethyl-9'-hydroxyspiroindolinenaphthoxadine
 • 1,3,3-trimethyl-9'-(2-hydroxyethyloxy)-spiroindolinenaphthoxadine
 • 1,3,3-trimethyl-6'-piperidino-9'-hydroxy-spiroindolinenaphthoxadine
 • 2-methyl-3,3'-spirobi[3H-naphtho[2,1-b]pyran] (2-Me)
 25 • 2-phenyl-3-methyl-7-methoxy-8'-nitrospiro[4H-1-benzopyran-4,3'-[3H]-naphtho[2,1-b]pyran
 • Spiro[2H-1-benzopyran-2,9'-xanthene]
 • 8-methoxy-1',3'-dimethylspiro(2H-1-benzopyran-2,2'-(1'H)-quinoline
 • 2,2'-Spirobi[2H-1-benzopyran]
 30 • 5'-amino-1',3',3'-trimethylspiro[2H-1-benzopyran-2,2'-indoline
 • Ethyl-β-methyl-β-(3',3'-dimethyl-6-nitrospiro(2H-1-benzopyran-2,2'-indolin-1'-yl)-propenoate

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- (1,3-propanediyl)bis[3',3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-indoline]
 - 3,3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'-benzoxazoline]
 - 6'-methylthio-3,3'-dimethyl-8-methoxy-6-nitrospiro[2H-1-benzopyran-2,2'-benzothiazoline]
 - (1,2-ethanediyl)bis[8-methoxy-3-methyl-6-nitrospiro[2H-1-benzopyran-2,2'-benzothiazoline]
 - N-N'-bis(3,3'-dimethyl-6-nitrospiro[2H-1-benzopyran-2,2'(3'H)-benzothiazol-6'-yl]decanediamide
 - α -(2,5-dimethyl-3-furyl)ethylidene(Z)-ethylidenesuccinic anhydride; α -(2,5-dimethyl-3-furyl)- α' , δ -dimethylfulgide
 - 2,5-diphenyl-4-(2'-chlorophenyl)imidazole
 - [(2',4'-dinitrophenyl)methyl]-1H-benzimidazole
 - N-N-diethyl-2-phenyl-2H-phenanthro[9,10-d]imidazol-2-amine
 - 2-Nitro-3-aminofluoren 2-amino-4-(2'-furanyl)-6H-1,3-thiazine-6-thione
4. A photochromic monomer according to Claim 1 wherein the polymerisable group is selected from the group consisting of olefins, allyls, polythiols, vinyls, acrylics and polyisocyanates.
5. A photochromic monomer according to Claim 1, wherein the organic spacer group S is selected from the group consisting of
- alkyl of 1 to 25 carbon atoms;
- alkoxy of 1 to 25 carbon atoms; and
- aryl or heterocyclic groups of 5 to 10 carbon atoms;
- with or without substituents selected from halogen, hydroxy, amine, acyl or carbonyl groups.
6. A photochromic monomer having the formula



wherein

n is an integer of 0 to 5;

m is an integer of 1 to 10;

P is a photochromic dye derivative of a photochromic dye selected from one or more of the group consisting of anthraquinones, phthalocyanines, spirooxazines, chromenes, pyrans including spiro-pyrans and fulgides;

- 5 R^1 and R^2 , which may be the same or different, are selected from hydrogen, halogen and an alkyl or substituted alkyl of 1 to 10 carbon atoms, or

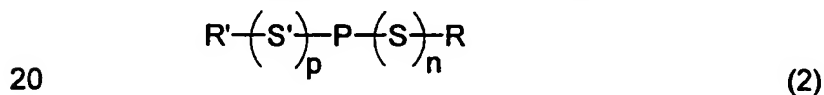
$\text{---}(\text{CR}^1\text{R}^2)_m\text{---}$ is an aryl or heterocyclic group of 5 to 10 carbon atoms; and

R^3 is selected from hydrogen, halogen, alkyl or substituted alkyl of 1 to 10 carbon atoms or alkoxy, or substituted alkoxy of 1 to 10 carbon atoms.

- 10 7. A photochromic monomer according to Claim 6, wherein R^1 , R^2 and R^3 are selected from the group consisting of hydrogen and alkyl of 1 to 5 carbon atoms.

8. A photochromic monomer according to Claim 6, selected from the group consisting of an ethoxy methacrylate derivative of 1,3-dihydrospiro[2H-anthra[2,3-d]imidazole-2,1'-cyclohexane]-5,10-dione, an acrylate derivative of 1,3,3-trimethyl-9'-hydroxyspiroindolenaphthoxadine, a methacrylate derivative of 1,3,3-trimethyl-9'-(2-hydroxyethoxy)-spiroindolenaphthoxadine and an acrylate derivative of 1,3,3-trimethyl-6'-piperidino-9'-hydroxyspiroindolenaphthoxadine.
- 15

9. A photochromic monomer having the formula



wherein

n and p are each integers of 0 to 5;

P is a photochromic dye moiety or derivative thereof;

- S and S', which may be the same or different, are each an organic
25 spacer group;

R and R', which may be the same or different, are each a polymerisable group.

10. A photochromic monomer according to Claim 9, wherein the photochromic dye moiety P is derived from a photochromic dye selected from one
30 or more of the group consisting of anthraquinones, phthalocyanines, spiro-

oxazines, chromenes, pyrans including spiro-pyrans and fulgides.

11. A photochromic monomer according to Claim 10, wherein the polymerisable groups R and R' are selected from olefins, allyls, polythiols, vinyls, acrylics and polyisocyanates.

- 5 12. A photochromic monomer according to Claim 11, wherein the organic spacer groups S and S' are each selected from the group consisting of
- alkyl of 1 to 25 carbon atoms, preferably 1 to 6 carbon atoms;
 - alkoxy of 1 to 25 carbon atoms, preferably 1 to 6 carbon atoms; and
 - aryl or heterocyclic groups of 5 to 10 carbon atoms;
- 10 with or without substituents selected from halogen, hydroxy, amine, acyl or carbonyl groups.

13. A cross-linkable polymeric casting composition including a photochromic monomer of the formula



wherein

n and p are each integers of 0 to 5;

P is a photochromic dye moiety or derivative thereof;

20 S and S', which may be the same or different, are each an organic spacer group;

R and R', which may be the same or different, are each a polymerisable group;

a diacrylate or dimethacrylate monomer; and

a polymerisable comonomer.

- 25 14. A photochromic monomer according to Claim 13, wherein the photochromic dye moiety P is derived from a photochromic dye selected from one or more of the group consisting of anthraquinones, phthalocyanines, spiro-oxazines, chromenes, pyrans including spiro-pyrans and fulgides.

- 15 15. A photochromic monomer according to Claim 14, wherein the
- 30 polymerisable group R and, when present, R' are selected from olefins, allyls,

polythiols, vinyls, acrylics and polyisocyanates.

16. A photochromic monomer according to Claim 15, wherein the organic spacer groups S and, when present, S' are each selected from the group consisting of

- 5 alkyl of 1 to 25 carbon atoms, preferably 1 to 6 carbon atoms;
 alkoxy of 1 to 25 carbon atoms, preferably 1 to 6 carbon atoms; and
 aryl or heterocyclic groups of 5 to 10 carbon atoms;

with or without substituents selected from halogen, hydroxy, amine, acyl or carbonyl groups.

- 10 17. A cross-linkable polymeric casting composition according to Claim 13, wherein the photochromic monomer is present in amounts of from approximately 0.001 to 55% by weight, based on the total weight of the casting composition.

18. A cross-linkable polymeric casting composition according to Claim 13, wherein the diacrylate or dimethacrylate monomer is a polyoxyalkyleneglycol
15 diacrylate or dimethacrylate.

19. A cross-linkable polymeric casting composition according to Claim 18, wherein the diacrylate or dimethacrylate component is present in amounts of from approximately 5 to 60% by weight, based on the total weight of the casting composition.

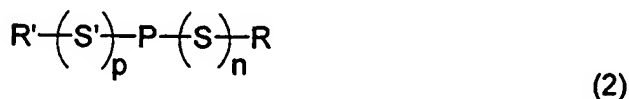
- 20 20. A cross-linkable polymeric casting composition according to Claim 13, wherein the polymerisable comonomer is selected from one or more of the group consisting of methacrylates, acrylates, vinyls, vinyl ethers, allyls, aromatic olefins, ethers, polythiols and epoxies.

21. A cross-linkable polymeric casting composition according to Claim 20,
25 wherein the polymerisable comonomer includes approximately 10 to 60% by weight, based on the total weight of the casting composition, of a high index bis-phenol monomer.

22. A cross-linkable polymeric casting composition according to Claim 20, wherein the polymerisable comonomer includes approximately 2.5% to
30 approximately 35% by weight, based on the total weight of the casting composition of a urethane monomer having 2 to 6 terminal acrylic and/or methacrylic groups.

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23. A photochromic coating composition including a photochromic monomer of the formula



5 wherein

n and p are each integers of 0 to 5;

P is a photochromic dye moiety or derivative thereof;

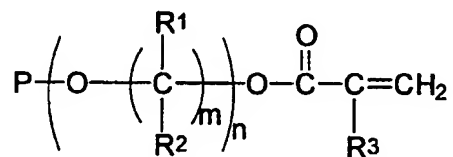
S and S', which may be the same or different, are each an organic spacer group;

10 R and R', which may be the same or different, are a polymerisable group;

a polymerisable co-monomer; and

a solvent therefor.

24. A photochromic coating composition according to Claim 23, wherein the
15 photochromic monomer is a monomer of the formula



wherein

P is a photochromic dye derivative of a photochromic dye selected from one or more of the group consisting of anthraquinones, phthalocyanines, spiro-oxazines, chromenes, pyrans including spiro-pyrans and fulgides;

n is an integer of 0 to 5;

m is an integer of 1 to 10;

R¹ and R², which may be the same or different, are selected from hydrogen, halogen and an alkyl or substituted alkyl of 1 to 10 carbon atoms, or

25 $\text{---}(\text{CR}^1\text{R}^2)_m\text{---}$ is an aryl or heterocyclic group of 5 to 10 carbon atoms; and

R³ is selected from hydrogen, halogen, alkyl or substituted alkyl of 1 to 10 carbon atoms or alkoxy, or substituted alkoxy or 1 to 10 carbon atoms;

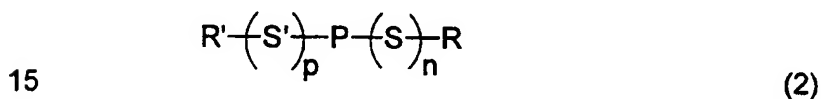
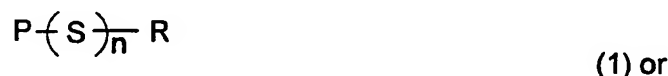
-32-

the photochromic monomer being present in amounts of from approximately 0.5 to 25% by weight, based on the total weight of the coating composition, excluding solvent.

25. A photochromic coating composition according to Claim 23, wherein the polymerisable comonomer is a UV curable low shrinkage monomer present in amounts of from approximately 65 to 95% by weight, based on the total weight of the coating composition, excluding solvent.

26. A coating optical article including an optical substrate; and a polymeric coating adhered to a portion of the optical substrate, the polymeric coating being formed from a photochromic coating composition including

a photochromic monomer of the formula



wherein

n and p are each integers of 0 to 5;

P is a photochromic dye moiety or derivative thereof;

S and S', which may be the same or different, are each an organic spacer group;

R and R', which may be the same or different, are a polymerisable group;

a polymerisable co-monomer; and

a solvent therefor.

27. A photochromic optical article formed from a cross linkable casting composition including

a photochromic monomer of the formula



wherein

n and p are each integers of 0 to 5;

P is a photochromic dye moiety or derivative thereof;

5 S and S', which may be the same or different, are each an organic spacer group;

R and R', which may be the same or different, are each a polymerisable group;

a diacrylate or dimethacrylate monomer; and

a polymerisable comonomer.

10

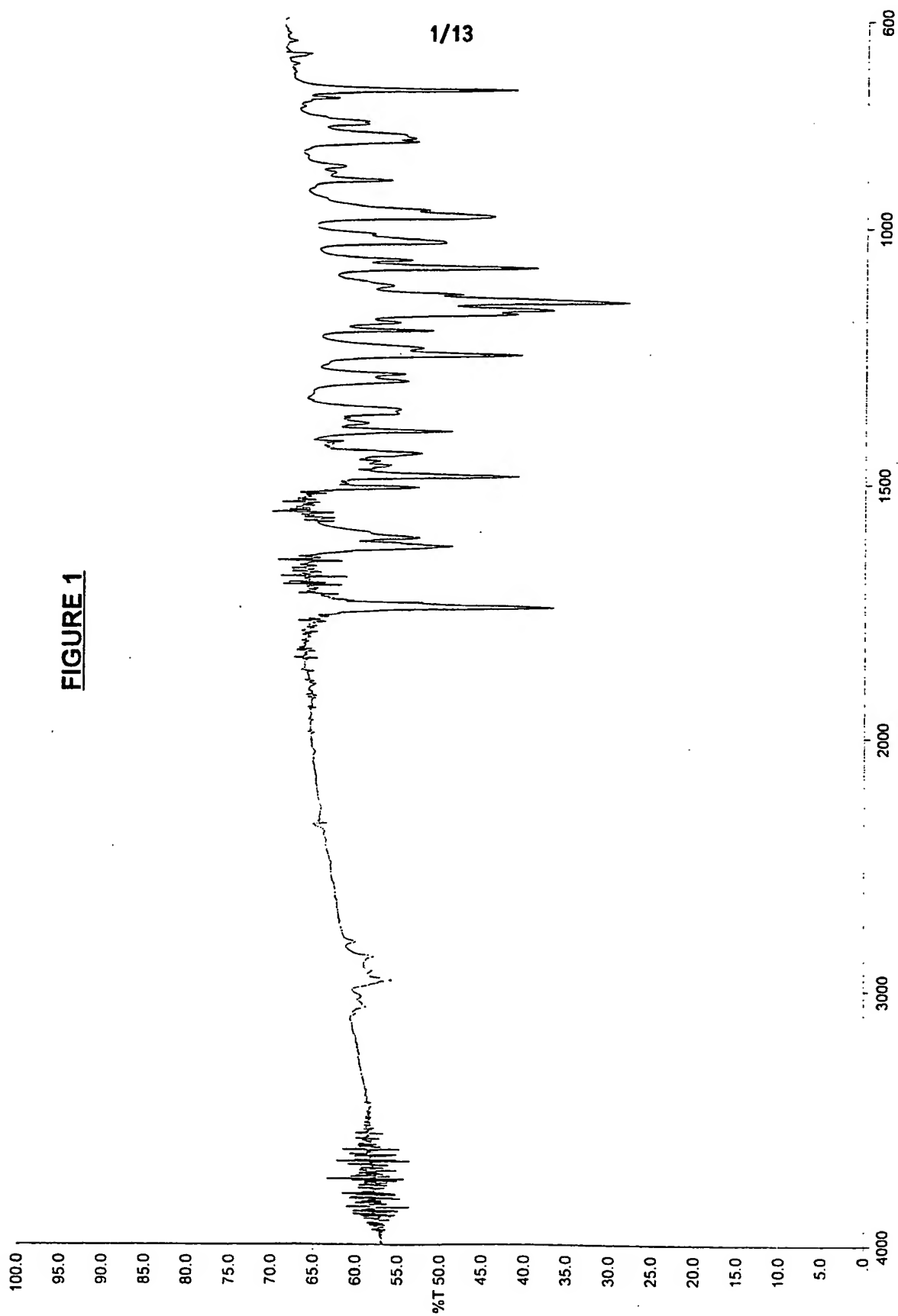


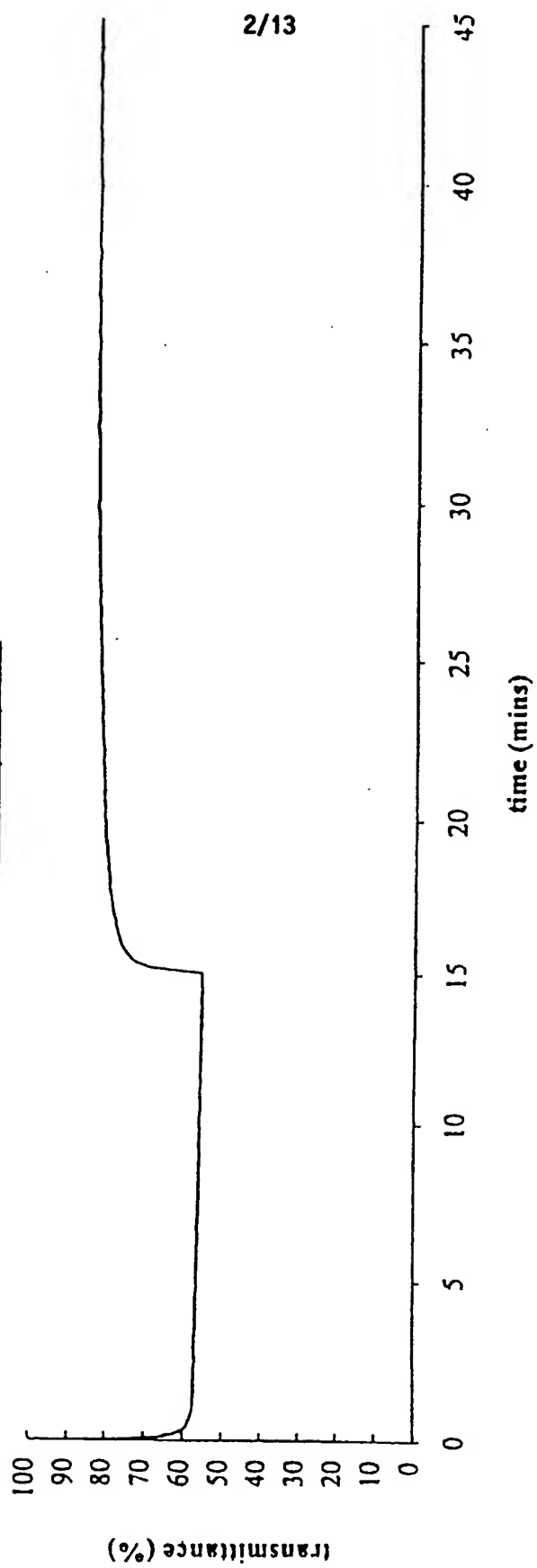
FIGURE 20.05% dye I (23°C)

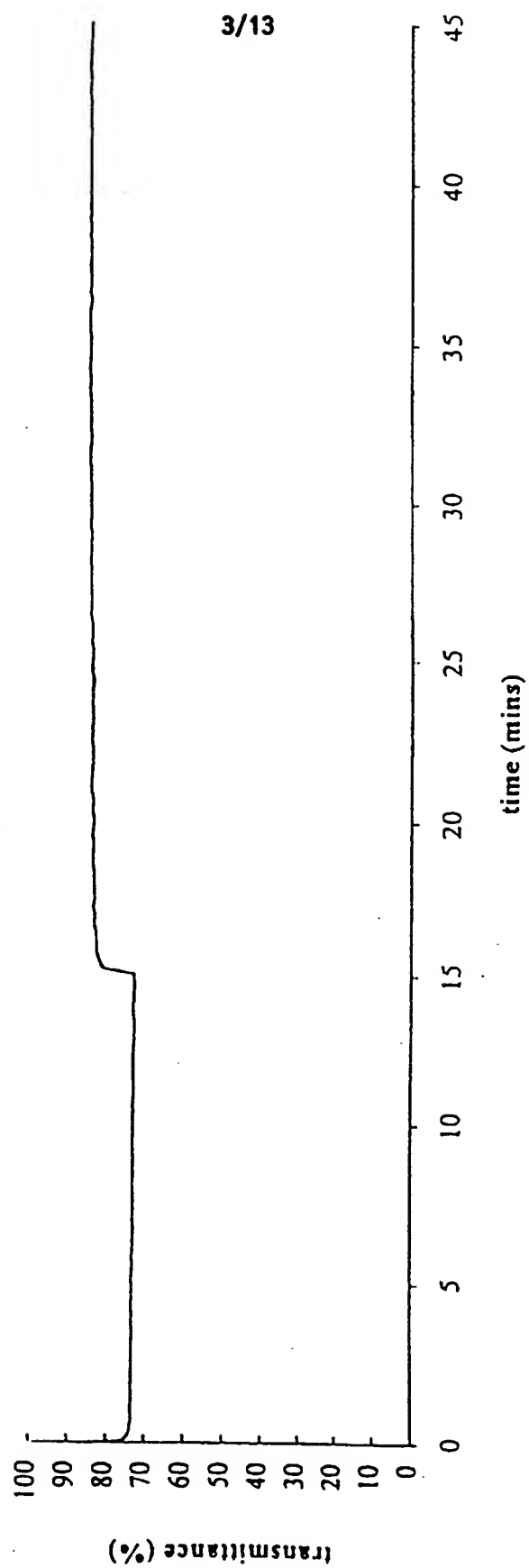
FIGURE 30.05% dye I (35°C)

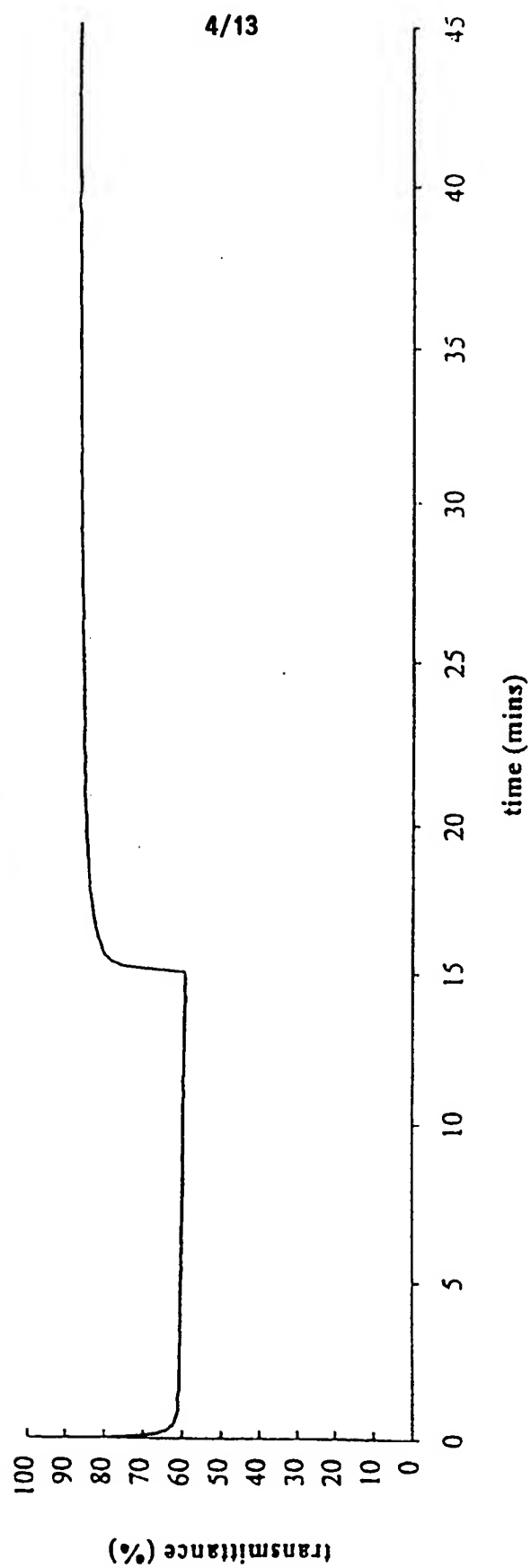
FIGURE 40.05% dye II (23°C)

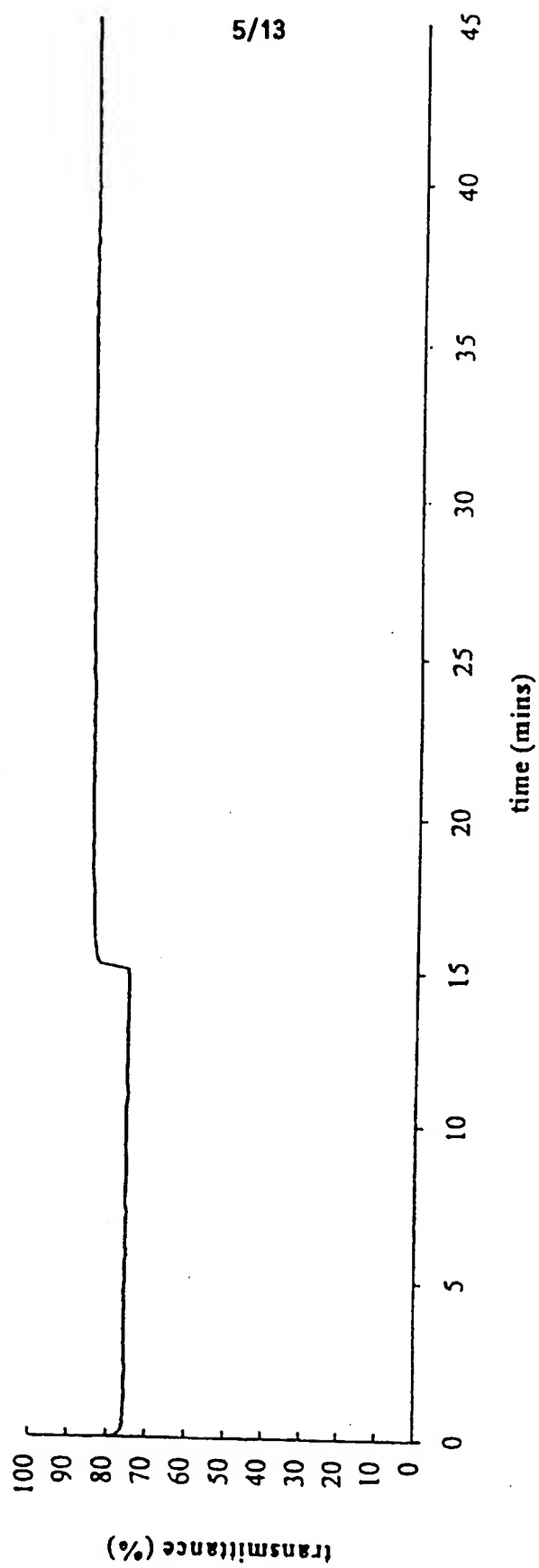
FIGURE 50.05% dye II (35°C)

FIGURE 6

0.05% polymerisable photochromic monomer (23°C)

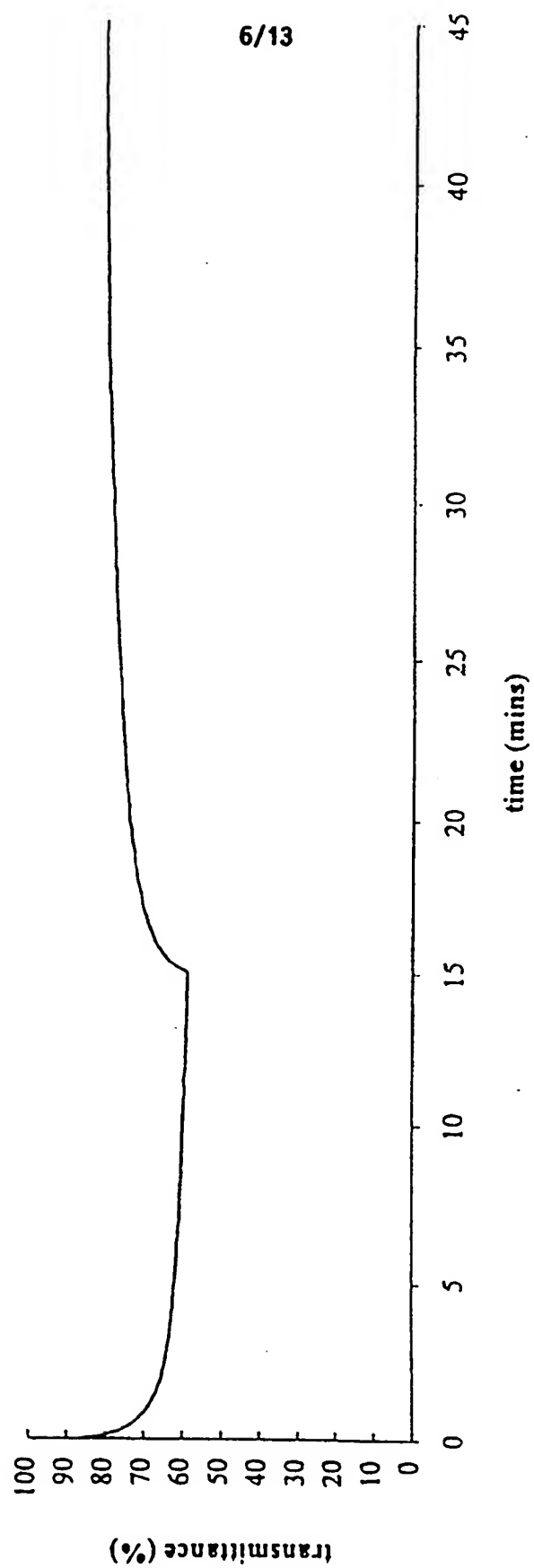


FIGURE 7

0.05% polymerisable photochromic monomer (35°C)

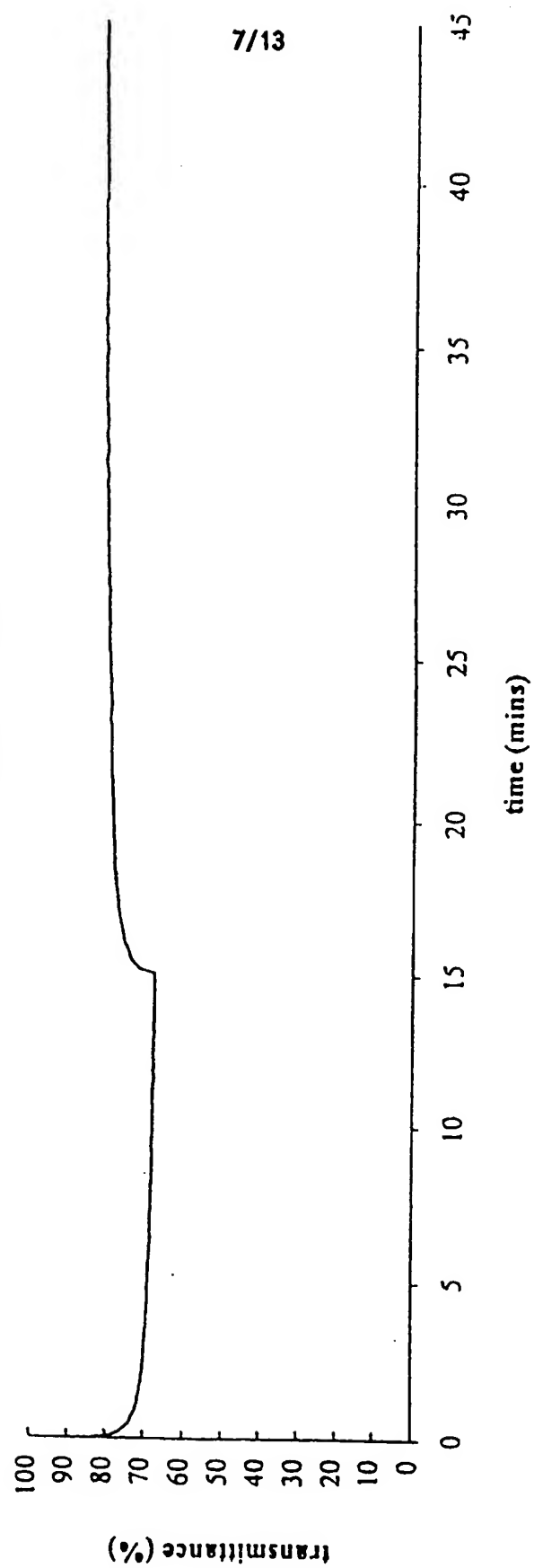


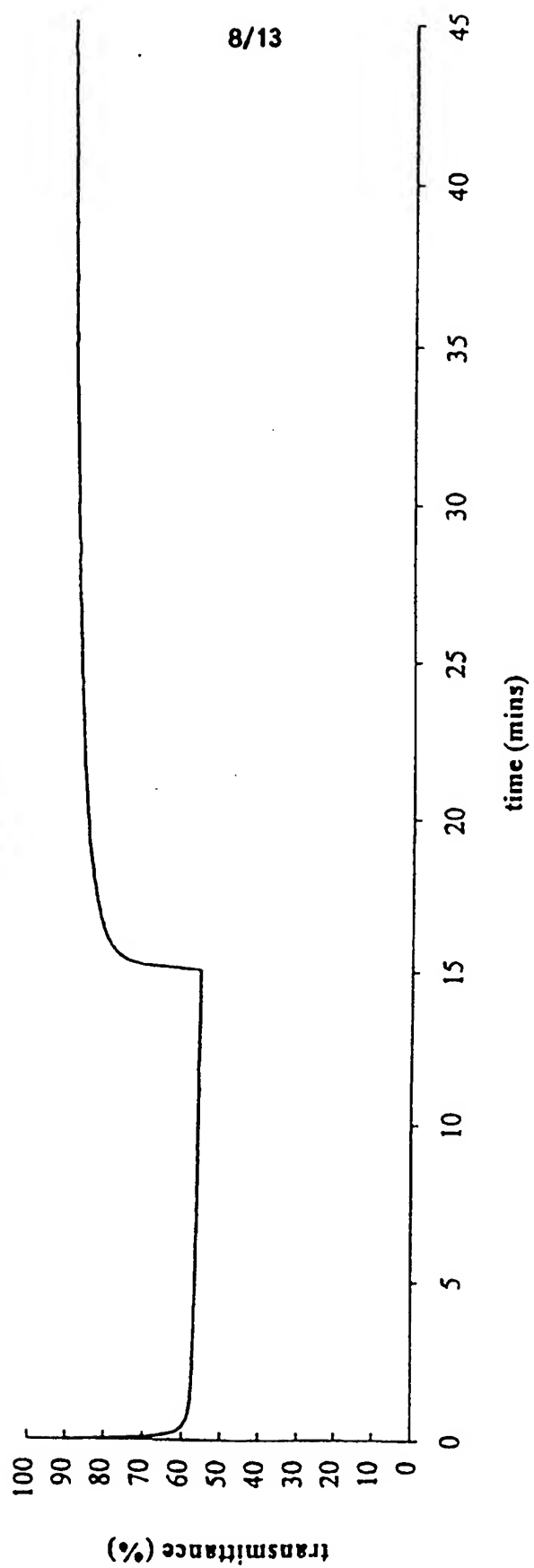
FIGURE 80.2% dye I (23°C)

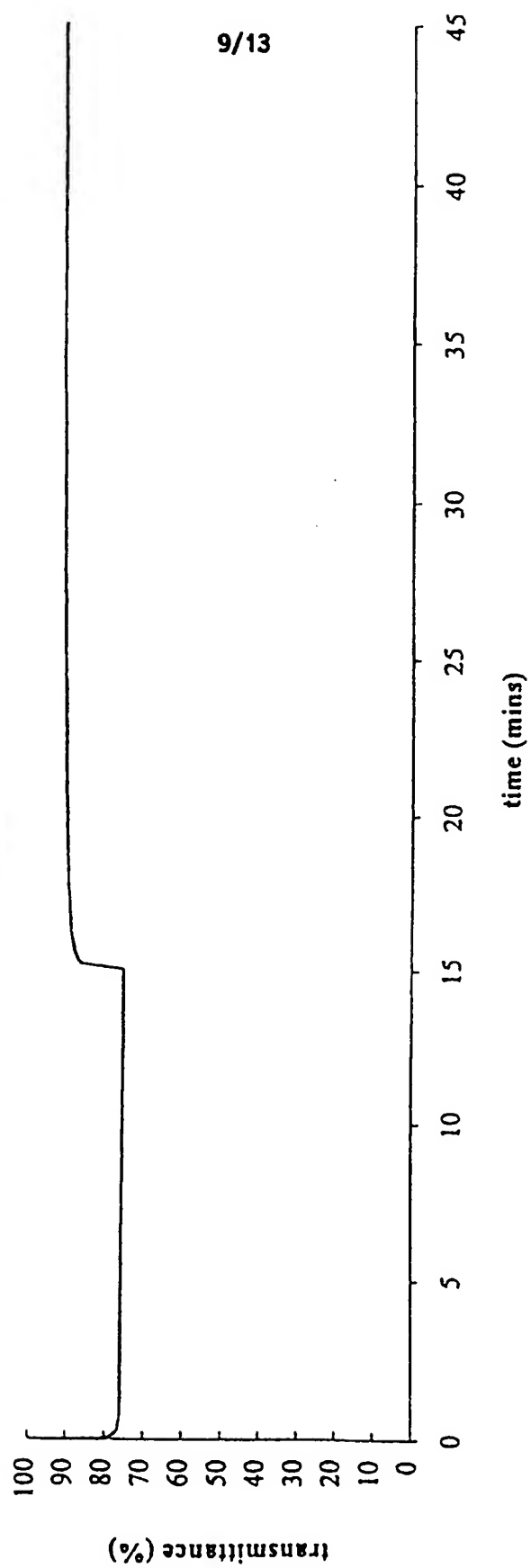
FIGURE 90.2% dye I (35°C)

FIGURE 10

0.2% polymerisable photochromic monomer (thermal cure) (23°C)

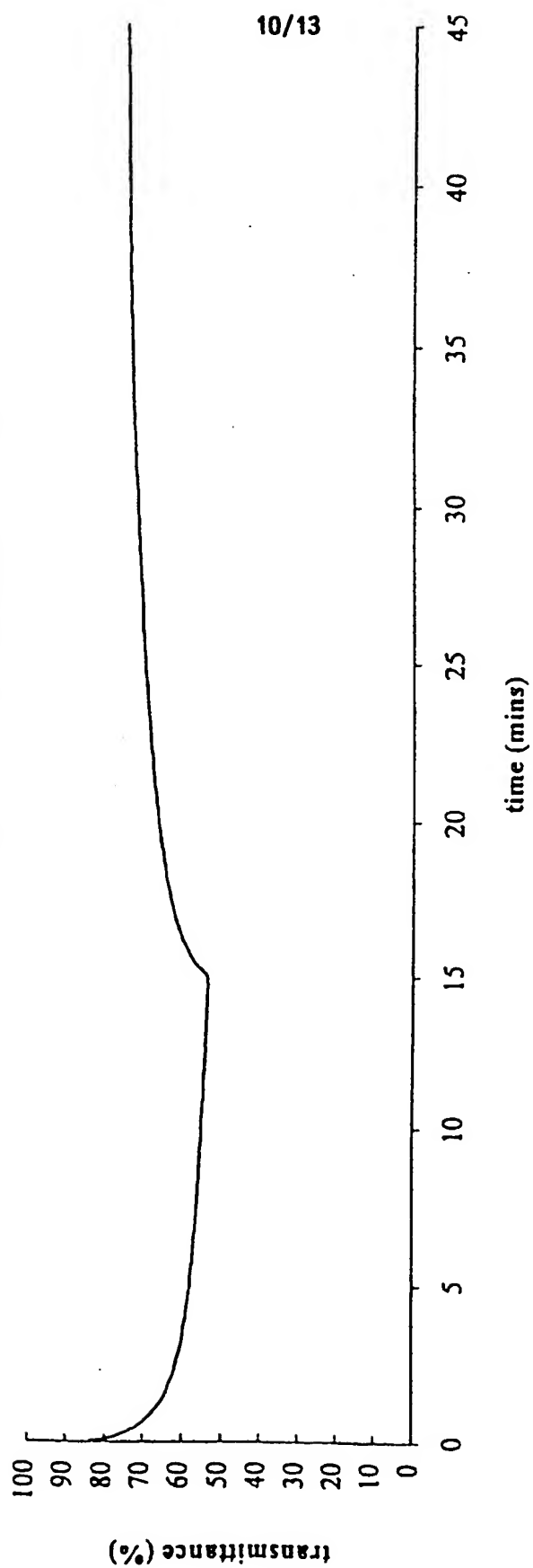


FIGURE 11

0.2% polymerisable photochromic monomer (thermal cure) (35°C)

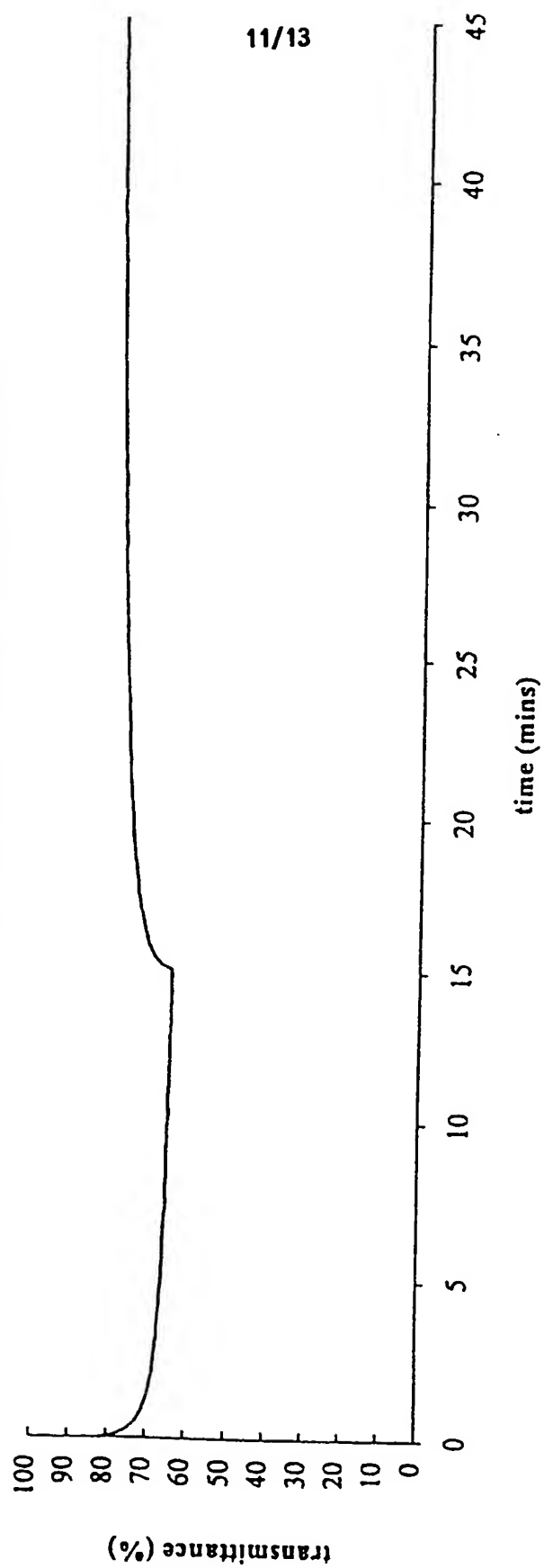


FIGURE 12

0.2% polymerisable photochromic monomer (UV cured) (23°C)

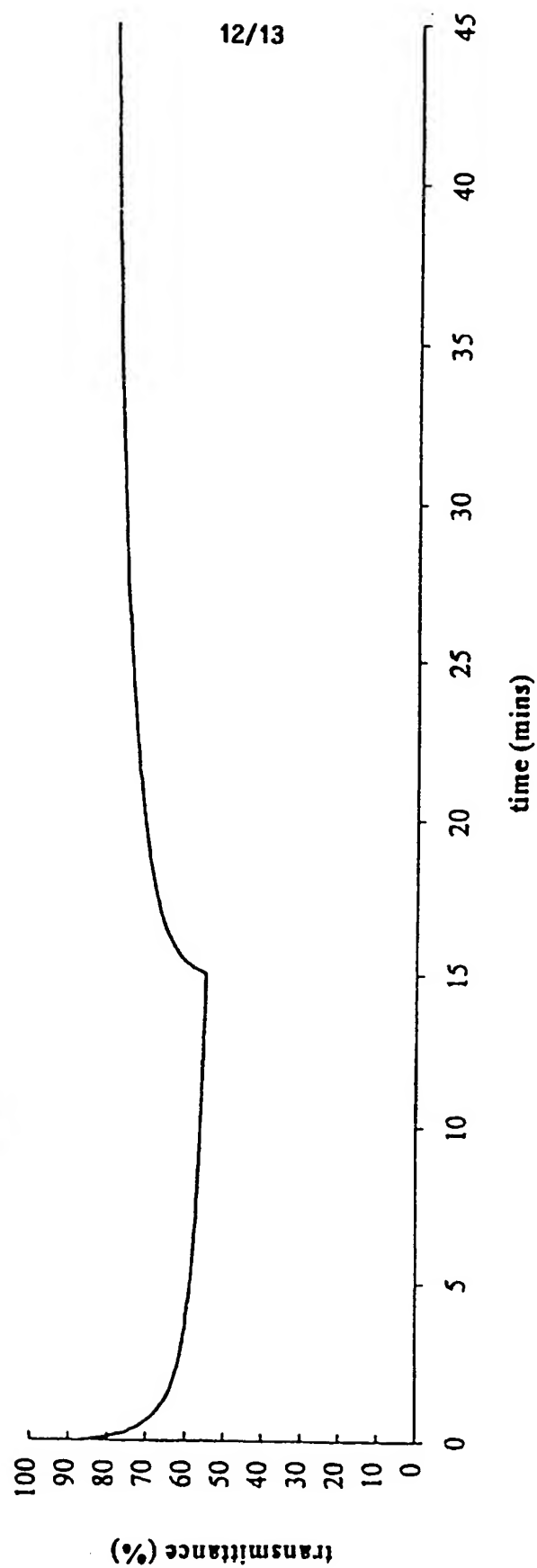
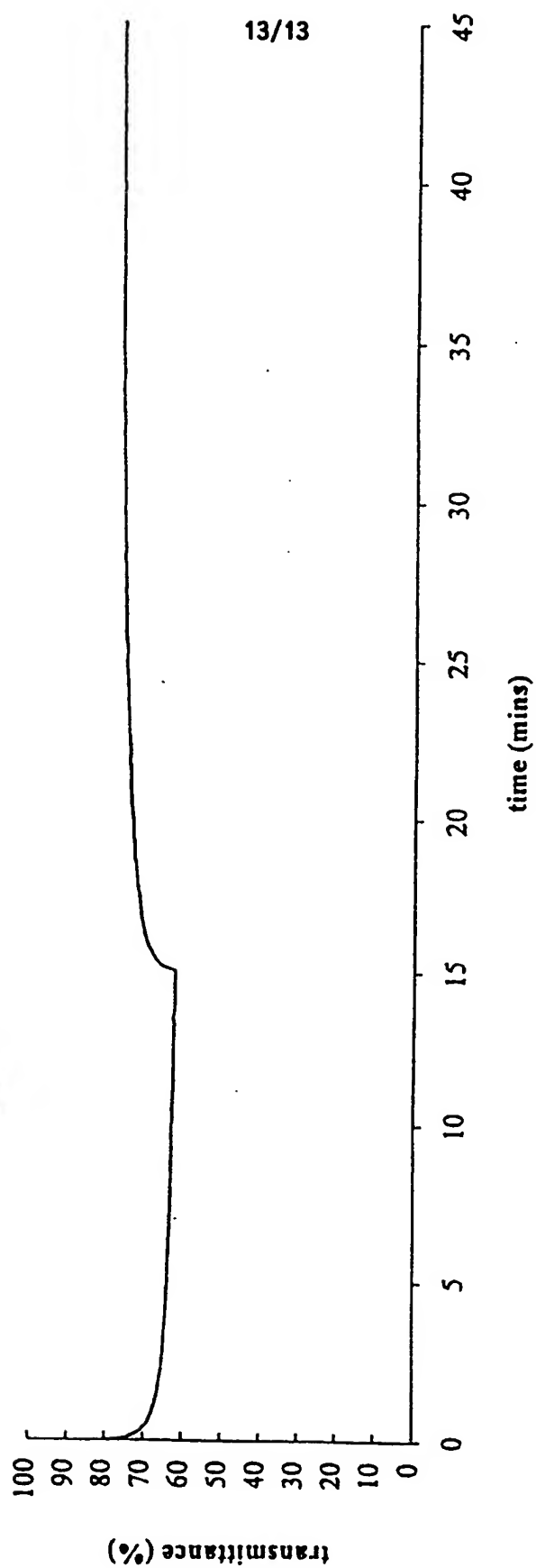


FIGURE 13

0.2% polymerisable photochromic monomer (UV cure) (35°C)



INTERNATIONAL SEARCH REPORT

International Application No.

PCT/AU 96/00466

A. CLASSIFICATION OF SUBJECT MATTER		
Int Cl ⁶ : C09K 9/02; C07D 235/02, 498/10; C08F 220/20, 220/28, 220/30, 246/00; G02B 1/10; G02C 7/10 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) IPC Keywords (photochrom:) and (polymer: or monomer:)		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) DERWENT: Keywords as above CAS Online: Substructure searches		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	US 5488119 A1 (FISCHER-REIMANN et al.) 30 January 1996 (see claims)	1-7, 13-27
X	US 5359085 A1 (IWAMOTO et al.) 25 October 1994 (see claims)	1-7, 13-27
X	US 5252742 A1 (MIYASHITA) 12 October 1993 (see claims)	1-7, 13-27
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 20 August 1996		Date of mailing of the international search report 17 SEPT 1996
Name and mailing address of the ISA/AU AUSTRALIAN INDUSTRIAL PROPERTY ORGANISATION PO BOX 200 WODEN ACT 2606 AUSTRALIA Facsimile No.: (06) 285 3929		Authorized officer G. A. Jenkins GILLIAN JENKINS Telephone No.: (06) 283 2252

INTERNATIONAL SEARCH REPORT

International Application No.
PCT/AU 96/00466

DOCUMENTS CONSIDERED TO BE RELEVANT		
C (Continuation)		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5236958 A1 (MIYASHITA) 17 August 1993 (see claims)	1-5, 13-23, 25-27
X	US 4986934 A1 (KWIATKOWSKI et al.) 22 January 1991 (see claims)	1-5, 13-23, 25-27
X	US 4929693 A1 (AKASHI et al.) 29 May 1990 (see claims and Examples)	1-27
X	EP 446717 A2 (BASF) 18 September 1991 (see claims)	1-5, 13-23, 25-27
X	Derwent Abstract Accession No. 93-240050/30, Class A12, JP 05/163324 A1 (SHOWA HIGH POLYMER) 29 June 1993	1-27
X	Derwent Abstract Accession No. 91-306996/42, Class A89, JP 03/205476 A1 (TORAY IND) 6 September 1991	1-7, 13-27
X	Derwent Abstract Accession No. 91-061989/09, Class A41, JP 03/011081 A1 (TORAY IND) 18 January 1991	1-27
X	Derwent Abstract Accession No. 90-088039/12, Class A41, JP 02/042084 A1 (TORAY IND) 13 February 1990	1-7, 13-27
A	Chemical Abstracts No. 84:180128, Zh. Org. Khim (1976), 12(1), 177-86 (GORELIK et al.) "Reaction of 1,2- and 2,3-diaminoanthraquinones with ketones and properties of anthraquinoneimidazolines"	3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/AU 96/00466

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report				Patent Family Member			
US	5488119	CA	2108291	EP	593397	JP	06/211731
US	5359085	AT	951215	DE	69023865	EP	420397
		JP	03/148258				
US	5252742	CA	2028777	DE	69027068	EP	411157
		WO	90/10007	JP	02/289580		
US	5236958	DE	69119507	EP	470264	WO	91/13072
US	4986934	CA	1000506	GB	1438830	NO	134331
		US	3823220	ZA	7305648		
US	4929693	DE	3852831	EP	277639	US	5166345
		JP	01/258681	JP	63/199279		
EP	446717	DE	4007636				
JP	05/163324	NONE					
JP	03/205476	NONE					
JP	03/011081	NONE					
JP	02/042084	NONE					
END OF ANNEX							